3 Experimental Studies

In accordance to the general objectives given in the introduction, a list of specific research objectives was derived. Experimental studies were done in the laboratory to investigate the different aspects outlined in the research objectives discussed below.

3.1 Research objectives

The research objectives of this dissertation project are to:

I) Evaluate the effectiveness of several pre-treatment methods, namely filtration, centrifugation and coagulation prior to membrane ultrafiltration. As the treated POME is still high in solid contents, the possibility of membrane fouling is high. As such, pre-treatment is normally required to improve the quality of feed as it is a convenient way to get rid of fouling (Persson, 1994),

II) Investigate the effect of pH and transmembrane pressure on ultrafiltration of pre-treated samples,

III) Investigate membrane rejection on feeds obtained using different pre-treatment methods,

IV) Study the overall efficiency of ultrafiltration with different pre-treatments.

3.2 Experimental methodology

The experimental part of this study followed the sequence as shown below. The details of the experimental procedures of each step are discussed in Section 3.3.

I) Sample collection

An adequate quantity of sample was collected from a palm oil mill in Banting. A portion of the raw sample was preserved according to the standard preservation techniques (refer Section 3.3.4) to be used for analysing the characteristics of the raw sample. Samples undergoing pre-treatments and membrane operations need to be maintained in their original state, as preservation by acidification will alter its characteristics.

II) Pre-treatment of samples

Three types of pre-treatment were applied separately to compare the effectiveness of each treatment. These treatments were:

A) Filtration

B) Centrifugation

C) Coagulation

A portion of each pre-treated sample was kept and preserved according to the standard preservation techniques (refer Section 3.3.4) for membrane feed characterisation.

III) Stirred-cell ultrafiltration

After pre-treatment, samples were ultrafiltered using a bench-scale stirred cell ultrafiltration unit. A few aspects were studied. The following parameters were investigated:

A) Pure water flux

Pure water flux characteristics for the membrane was obtained by filtering deionised water at an increment of every 1 bar of transmembrane pressure (from 1 bar to 7 bar).

B) Sample Flux

Flux for each pre-treated sample was obtained for comparison purpose. The flux was observed in the range of 1 bar to 7 bar of transmembrane pressure.

C) Variation of pH value of sample

In order to investigate the effect of pH value on rejection characteristics (COD, total solids, suspended solids, ammoniacal nitrogen, total nitrogen and colour), ultrafiltration of filtered and centrifuged samples were done at two different pH values at transmembrane pressures of 4.5 bar and 7.0 bar. The two pH values were pH 8 (original value of effluent) and pH 2.2 (pH at isoelectric point of cellulose membrane)(Bowen and Clark, 1984).

Ultrafiltration of the sample that was pre-treated with coagulation technique was lastly carried out at the pH value that gave better rejection characteristics on the filtratered and coagulated samples. This is to improve experimental efficiency. As the better pH value is already known from the previous analysis on samples pre-treated with filtration and centrifugation, it could be applied directly on coagulated samples to save hassles.

Permeate from each run of ultrafiltration was kept and preserved accordingly for membrane permeate characterisation.

D) Variation of transmembrane pressure

To study the effect of pressure on rejection characteristics, samples pre-treated using filtration and centrifugation methods were ultrafiltered at 2 different values of TMP. Duplicate runs for each sample at TMP of 4.5 bar and 7.0 bar were undertaken. The TMP that gave the better rejection characteristics was then applied for ultrafiltration of the sample that was pre-treated using the coagulation technique. Permeate from each run of filtration was kept and preserved accordingly for membrane permeate characterisation.

IV) Characteristic analysis of samples

In order to evaluate the efficiency of membrane ultrafiltration, selected parameters were chosen to characterise the various samples (raw, pre-treated and permeate). These parameters are of great importance for effluent characterisation and the values need to meet the level of statutory discharge limits in the Environmental Quality Act (Prevailing Effluent Discharge Standards for Crude Palm Oil Mills, 1984) before being released into watercourses. The parameters are Chemical Oxygen Demand (COD), Ammoniacal Nitrogen (AN), Total Kjeldahl Nitrogen (TKN), suspended solids (SS), turbidity and colour.

A) Chemical Oxygen Demand, COD

COD is the measurement of the total quantity of oxygen required for oxidising organic matters to carbon dioxide and oxygen. It gives an idea of the organic strength of wastewater. This parameter helps to indicate toxic condition and the presence of biologically resistant organic substances.

B) Ammoniacal Nitrogen, AN

Ammonia is the product of microbiological decay of animal and plant proteins. It is a toxic gas and competes for the space in the water that is normally occupied by dissolved oxygen (Jackson, 1993). Thus, ammoniacal nitrogen determination gives a rough estimate of dissolved-oxygen condition in the water.

C) Total Kjeldahl Nitrogen, TKN

Total Kjeldahl Nitrogen is the sum of free ammonia and organically bound nitrogen compounds, which are converted to ammonium sulfate under conditions of acid digestion and heat. Ammonia and organic nitrogen analysis are important in determining the amount of nitrogen released. As nitrogen is a nutrient for the growth of microorganisms, a high nitrogen content will cause eutrophication in receiving watercourses.

D) Suspended Solids, SS

Suspended solids determination is an important parameter during analysis of polluted waters. Deposition of solid in quiescent stretches of a stream will impair the normal aquatic life of the stream. Sludge blankets containing organic solids will undergo progressive decomposition resulting in oxygen depletion and the production of noxious gas (Eckenfelder, 1989).

E) Colour and Turbidity

Colour and turbidity present aesthetic problems even though they may not be particularly deleterious for most water uses.

3.3 Experimental procedures

This section gives a detailed account of the experimental procedures carried out as well as the necessary materials and equipment associated with each step of the experiment.

3.3.1 Sample collection

The treated palm oil mill effluent was obtained from a palm oil mill in Banting as the primary feed sample.

10 litres of effluent was collected each time at the discharge point of a palm oil mill effluent recycling pond. This pond receives palm oil mill effluent (POME), which is sufficiently treated by anaerobic reactor-cum-aerated lagoon system, and should comply with the prevailing effluent discharge standards for crude palm oil mill required by the Environmental Quality Act. Instead of releasing it into watercourses, the treated POME is stored in this pond for reuse purposes i.e. to be utilized as feed for hydrocyclone or as wash waters.

This sampling point was chosen instead of the final treatment pond as the final treatment pond may contain POME which is not totally biodegraded and hence do not reach the legislative discharge standard. No composite sample was taken at different points of the recycling pond. This is because the recycling pond is continuously receiving discharge, thus there is a mixture of freshly treated effluent and old effluent. This results in a heterogeneous effluent quality that is not desired in the study.

The sample collected was stored in a covered polyethylene container and brought back to the laboratory for analysis. The pH value of the sample was measured on the spot.

3.3.2 Pre-treatment of samples

I) Filtration

The sample was filtered using a set of filtration apparatus consisting of filter paper Whatman #1, a one litre filtering flask, a porcelain filtration funnel and an Emerson vacuum pump (Model no. SA55JXHTP-4698).

The filter paper was washed initially by pouring through it three successive 20 ml volumes of distilled water under vacuum suction to remove any dirt and impurities. Traces of water were removed by applying vacuum for an additional two minutes.

200 ml of sample was then poured into the funnel for filtration. The filtered sample collected in the filtering flask was transferred into a clean stoppered glass bottle for storage.

II) Centrifugation

A Jouan bench-top centrifuge (Model BBVV) was used to separate constituents of different specific gravity in the sample.

The raw sample was pipetted into ten 10-ml centrifugation tubes and placed inside the fixed-angle rotor. Rotation was allowed for 10 minutes at a rotational speed of 2 500 r.p.m., producing a centrifugal force equivalent to 1250 x *g*.

After centrifugation, the supernatant of the sample was pipetted into a clean glass container for storage while the sludge was disposed.

III) Coagulation

A simple jar test was carried out to determine the most suitable coagulant and its dosage. Two coagulants were tested, which were ferrous sulphate ($FeSO_4.7H_2O$) and ferric sulphate ($Fe_2(SO_4)_3$). A flocculant of cationic nature, P 852, was used in this study. A stock solution of 10 000 p.p.m. (1%) was prepared for each coagulant and the flocculant.

A Phipps & Bird Stirrer (Model no. 7790-402) was utilised for stirring and mixing. Six two-litre-beakers were used. One litre of sample was transferred into each beaker. The first beaker acted as control and thus do not contain any chemicals. Ferrous sulphate was added into the second and third beaker in subsequent volumes of 25 ml and 27.5 ml respectively. Ferric sulphate measuring 20 ml, 25 ml and 25 ml were added into the last three beakers respectively. The amount of ferric sulphate used was less, as ferric ion is a trivalent cation and thus is expected to be a better coagulant compared with ferrous sulphate.

When the addition of coagulant was completed, rapid mixing was set for 3 minutes, at a stirring speed of 155 r.p.m.. After 3 minutes of rapid mixing, 10 ml of flocculant was added into each beaker except for the last beaker that contained 25 ml of ferric sulphate. This was done to evaluate the effect of the presence of flocculant. Slow stirring then followed the rapid mixing stage. The slow stirring phase lasted for 30 minutes with the stirrer rotating at 25 r.p.m..

When the whole stirring process was completed, samples were left for 30 minutes to allow the flocs to settle. Then, the supernatant was collected and evaluated in terms of colour, turbidity and suspended solids according to the analytical procedures in Section 3.3.5. The volume of floc produced for each beaker was also observed.

The coagulant that produced the supernatant with the best quality and produced the least floc was then tested again using higher coagulant concentration. The optimum coagulant concentration obtained in the experiment was applied to treat the raw samples.

3.3.3 Membrane ultrafiltration

Pre-treated raw samples were ultrafiltered using Spectrum Molecular/Por Stirred Cell (Model no. 20062). The set up for this equipment is shown in Figure 3-1. A 76-mm Spectrum Cellulose Ester Disc Membrane with MWCO of 5 000 was used as the filter media. Pressure was achieved through the input of oxygen-free nitrogen.

A new membrane was soaked overnight in deionised water to remove the water-soluble protective coating on the membrane surface.

Pre-treated samples were divided into 2 portions, where one portion was preserved as membrane feed and later analyzed, while the other was used in the ultrafiltration test.

I) Flux test

A volume of 100 ml of pre-treated sample was poured into the stirred cell. The top plate containing a pressure relieve valve and gas inlet port was placed on top of the cell and secured with a clamp. To apply pressure into the cell, the pressure relieve valve was closed and the pressure valve supplying oxygen-free nitrogen was opened. The pressure valve was adjusted to the desired pressure indicated by the pressure gauge.

A 10-ml measuring cylinder was placed at the outlet of the stirred-cell to collect the permeate. When the pressure achieved the desired level, a quantity of 5 ml of permeate was collected and the time needed to collect it was recorded. When the permeate reached 5 ml, the pressure valve was closed and the pressure relieve valve was then opened to release the pressure accumulated in the cell.

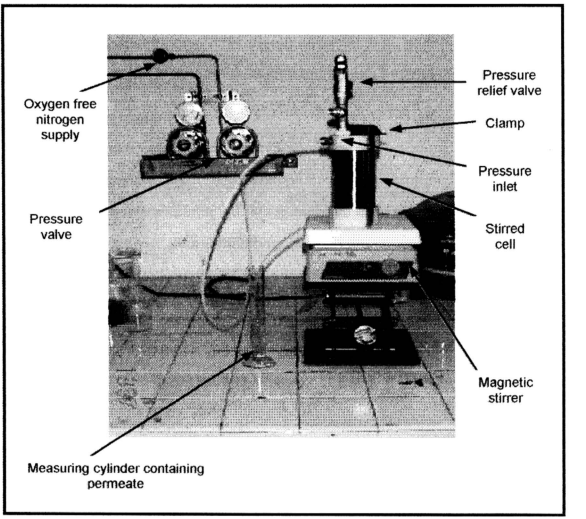

Figure 3-1 Laboratory set up for the stirred-cell experiment

This procedure was repeated for different applied pressure ranging from 1 bar to 8 bar. The desired transmembrane pressure was obtained by subtracting the atmospheric pressure (1 bar) from the applied pressure. In order to preserve the microenvironment in the cell, the permeate collected was poured back into the feed reservoir after every 2 runs of filtration. This action ensured that feed concentration throughout the flux test was maintained.

II) Variation of transmembrane pressure

The procedure to obtain the flux at two different TMP of 4.5 bar and 7.0 bar followed the same steps as described in Section 3.3.3 (I) above.

III) Variation of pH value

The ultrafiltration tests were done at two different pH values, i.e. at pH 2.2 and pH 8. The value of pH 8 was the original pH of the raw sample. It did not vary after pre-treatments. The value of pH 2.2 was achieved by the addition of sulphuric acid (ACS grade).

3.3.4 Sample preservation

Sample preservation was necessary to maintain the original state of the sample. In this study, samples were preserved according to the *Federal Register*, July 1, 1995, 40 CFR, Part 136.3 adapted from *Hach Water Analysis Handbook 3rd Ed.*

Raw, pre-treated and ultrafiltered samples were preserved immediately after completion of each treatment procedure. This was done with the addition of sulphuric acid to a pH value lower than pH 2. Acidified samples were then kept in the refrigerator at a temperature of 4°C. All samples were kept in glass bottles.

3.3.5 Analytical procedures

To assess the effectiveness of different treatments, samples were analysed for its characteristics before and after each treatment.

Chemical analyses were carried out on raw sample, samples before and after each pre-treatment, the feed and permeate of ultrafiltration at different operating conditions.

All analyses were carried out using Hach analytical chemical equipment as explained below.

I) Chemical Oxygen Demand, COD

Samples were analysed for COD values using the Hach Colorimetric Measurement, Method 8000, as outlined in the *Hach Water Analysis Handbook 3rd Ed.* This method is registered under *Federal Register*, April 21 1980, 45 (78), 26811-26812, and accepted for reporting by the U.S. Environmental Protection Agency.

Reagents and apparatus included the Hach High Range COD Reagent (Cat. no. 21259-25, capable of measuring COD in the range of 0 to 1500 mg/L COD), Hach COD Reactor and Hach DR/3000 Spectrophotometer. Picture of these apparatus is given in Figure 3-2.

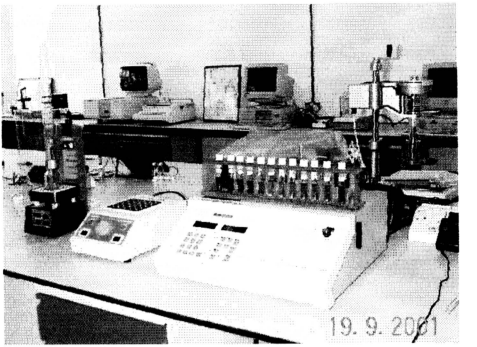

Figure 3-2 Hach Water Analysis Apparatus (From left Digesdahl Digestion Apparatus, COD Reactor and DR/3000 Spectrophotometer)

A) Digestion

The samples to be tested needed prior digestion using the Hach COD Reactor.

Samples were homogenised by shaking vigorously in a tightly covered container. At the same time, the Hach COD Reactor was turned on and preheated to 150°C in a fume cupboard.

The cap of COD Digestion Reagent Vial was removed with vial held slanting at an angle of 45°. 2.00 ml of sample was pipetted into the vial. Vial cap was then replaced and closed tightly. The vial was rinsed with deionised water and wiped clean with a paper towel. It was then held by the cap and inverted several times to mix the contents. Finally, the vial was placed in the preheated COD reactor.

One blank was prepared using the same procedure substituting deionised water for sample. All the vials filled with samples were placed in the COD reactor and heated for 2 hours. Digested samples were left to cool to room temperature before the following colorimetric measurements were carried out.

B) Colorimetric measurement

Colorimetric measurement was done using Hach DR/3000 Spectrophotometer.

Stored programme number **46** was entered, and the button **Stored Programme** pressed. Wavelength was adjusted to **620 nm** as indicated by the screen, and the **Clear** button was pressed.

The COD vial adapter was placed into the cell holder with the hole facing source of light. The outside of the blank vial was wiped and the vial placed into the adapter, then covered with adapter cover. **Zero concentration** was pressed. The blank was read as a standard containing 0 mg/L COD. The Auto Update button will be lighted up, indicating the function was on.

The blank was then removed and samples were placed into the adapter one at a time. The screen then automatically displayed the value of COD in mg/L once every sample was inserted and properly covered.

II) Ammoniacal Nitrogen, AN

Samples were analysed for AN values using the Hach Nitrogen Ammonia High Range Test 'N Tube Salicylate Method, Method 10031, as outlined in the *Hach Water Analysis Handbook 3rd Ed.*. This method is adapted from *Clin. Chim. Acta* 14:403 (1996).

The ammoniacal nitrogen content of sample was measured using Am Ver Reagent Set High Range Test 'N Tube (Cat. no. 26069-00, capable of measuring 0 to 50.0 mg/L NH_3-N) and Hach DR/3000 Spectrophotometer.

The wavelength for ammoniacal nitrogen was set to **655 nm** and the **Clear** button was pressed. Caps were removed from the vials. 0.1 ml of sample was pipetted into each vial. The content of one Ammonia Salicylate Reagent Powder Pillow was added into each vial. Following this, the content of one Ammonia Cyanurate Reagent Powder Pillow was added into each vial. Vials were capped tightly and shaken vigorously to dissolve the powder.

One blank was prepared using the same procedure substituting deionised water in place of the sample. After all vials for samples were ready, the **20 Timer** button was pressed. This allowed a 20 minutes reaction period to take place.

The COD vial adapter was placed into the cell holder. When the timer beeped, the vial that contained the blank was placed into the vial adapter and covered. The **Manual Programme** button was pressed followed by **Zero**. The concentration factor of **35.42** was then entered, and **Concentration Factor** pressed. Lastly, the **1 Concentration** button was pressed. The Auto Update button lighted, indicating that the function was on.

The blank was then removed and the samples were placed into the adapter one at a time. The screen automatically displayed the values of ammoniacal nitrogen in mg/L once every sample was inserted and properly covered.

III) Total Kjeldahl Nitrogen, TKN

The samples were analysed for TKN values using Hach Nitrogen, Total Kjeldahl Nessler Method, Method 8075, as outlined in the *Hach Water Analysis Handbook 3rd Ed.* This method is adapted from Hach et al. *Journal of Association of Official Analyticl Chemists*, 70(5)783-787(1987); Hach et al. *Journal of Agricultural and Food Chemistry*, 33(6) 1117-1123(1985); *Standard Methods for Examination of Water and Wastewater.*

Chemical analysis of TKN was carried out using Total Kjeldahl Nitrogen Reagent Set (Cat. no. 24953-00, capable of measuring 0 to 150 mg/L TKN), Hach Digesdahl Digestion Apparatus and Hach DR/3000 Spectrophotometer. Picture of Hach Digesdahl disgestion apparatus is given in Figure 3-2.

A) Digestion

The samples were first digested using the Hach Digesdahl Digestion Apparatus. The Digesdahl Digestion Apparatus was preheated in a fume cupboard. 10 ml of sample was pipetted into a digestion flask. Then, 3 ml of sulfuric acid was added into the digestion flask. A few boiling chips were added to stabilize the boiling solution. The digestion flask was then placed in the Digesdahl at the temperature of 440°C, which is the boiling point of sulfuric acid. This solution was heated to the preset temperature.

On reaching the desired temperature, a boiling time of 5 minutes was observed with a stopwatch. After 5 minutes, 16.7 ml of hydrogen peroxide (30%) was added through the funnel on top of the digestion apparatus. When all the hydrogen peroxide dripped into the solution, a one-minute reaction period was allowed using a stopwatch.

After one minute, the digestion flask was removed from the Digesdahl apparatus and allowed to cool to room temperature for the following colorimetric analysis.

One blank was prepared using the same procedure, substituting deionised water for the sample.

B) Colorimetric measurement

Colorimetric measurement was done using the Hach DR/3000 Spectrophotometer. Stored programme number **42** was entered, and the **Stored Programme** button pressed. The wavelength was adjusted to **460 nm** as indicated by the screen, and **Clear** button was pressed.

The solution in the digestion flask was diluted into 100 ml with distilled water. 2 ml of diluted sample and blank was pipetted into two separate 25-ml volumetric flasks. 1 drop of TKN Indicator was added into each flask. A few drops of KOH (8.0 N) was added and mixed until the first apparent blue colour was visible. Both volumetric flasks were then filled to a pre-marked 20-ml indicator with distilled water.

Three drops of Mineral Stabiliser were added to each flask. The flasks were inverted several times to mix the contents. Then, 3 drops of Polyvinyl Alcohol Dispersing Agent were added to each flask. The flasks were inverted several times to mix the contents. Both flasks were filled with distilled water to the 25-ml mark. 1 ml of Nessler Reagent was pipetted into each flask. Lastly, the flasks were stoppered and inverted repeatedly.

The **2 Timer** button was pressed. A two minutes reaction period then began. When the timer beeped, content of each flask was poured into two separate 25-ml sample cells. The sample cell containing blank solution was placed into the cell holder and the light shield closed. The **Zero concentration** button was pressed. This read the blank as a standard containing 0 mg/L TKN. The Auto Update button lighted, indicating the function is on.

The blank was then removed and the samples were subsequently placed into the adapter. The screen automatically displayed the value of Total Kjeldahl Nitrogen in mg/L once every sample was inserted and properly covered.

IV) Suspended solids, SS

The suspended solids content was measured using Hach Solids, Suspended Photometric Method, Method 8006 as outlined in the *Hach Water Analysis Handbook 3rd Ed.* It is adapted from *Sewage and Industrial Wastes*, 31, 1159 (1959).

A Hach DR/3000 Spectrophotometer was used in this analysis. Stored programme number **52** was entered, and the **Stored Programme** button was pressed. The wavelength was adjusted to **810 nm** as indicated by the screen, and the **Clear** button was pressed.

25-ml of sample was poured into a sample cell. A blank was prepared by substituting deionised water for the sample. The blank was placed in the cell holder and the light shield closed. The **Zero Concentration** button was pressed. This read the blank as a standard containing 0 mg/L suspended solids. The Auto Update button was then lighted up, indicating that the function was on.

The blank was then removed and samples were subsequently placed into the adapter. The screen automatically displayed the values of suspended solids in mg/L once every sample was inserted and properly covered.

V) Turbidity

Turbidity was measured using Hach DR/3000 Spectrophotometer.

Stored programme number **59** was entered, and the **Stored Programme** button was pressed. The wavelength was adjusted to **450 nm**, and the **Clear** button pressed.

25-ml of sample was poured into a sample cell. A blank was prepared by substituting deionised water for the sample.

The blank was placed in the cell holder and the light shield closed. The **Zero Concentration** button was pressed. This read the blank as a standard with turbidity measurement of 0 FTU. The Auto Update button lighted, indicating the function is on.

The blank was then removed and samples were subsequently placed into the adapter. The screen automatically displayed the value of turbidity in FTU once every sample was inserted and properly covered.

VI) Colour

The colour content of sample was determined using Hach Color APHA Platinum-Cobalt Standard Method, Method 8025 as outlined in the *Hach Water Analysis Handbook 3rd Ed.* It was adapted from the *Standard Methods for the Examination of Water and Wastewater.*

The analysis was done with Hach DR/3000 Spectrophotometer. Stored programme number **16** was entered, and the **Stored Programme** button was pressed. The wavelength was adjusted to **455 nm**, and the **Clear** button pressed.

25-ml of sample was poured into a sample cell. A blank was prepared by substituting deionised water for sample.

The blank was placed in the cell holder and light shield closed. **Zero Concentration** was pressed. This read the blank as a standard with a colour measurement of 0 PtCo APHA. The Auto Update button lighted, indicating the function is on. The blank was then removed and samples were subsequently placed into the adapter. The screen automatically displayed the value of colour content in PtCo APHA once every sample was inserted and properly covered.